Reconfigurable Assemblies of Plasmonic Nanoparticles and Proteins for Biosensing

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Generating assemblies of gold nanoparticles with tailored localized surface plasmon resonance (LSPR) is a winning strategy for designing ultrasensitive biosensors [1] and photothermal nanomedicines [2]. If these assemblies changed their structure as a function of external stimuli, they could adapt their LSPR to variations in physicochemical cues. Such materials could be programmed to detect changes in their environment and emit signals and/or exert a therapeutic effect autonomously.

In this contribution I will show a new method for assembling gold nanoparticles with tailored near-infrared (NIR) LSPR that sense changes in chemical cues and reconfigure their structure accordingly [3]. It is based on adding biotin-binding proteins to a solution of citrate-capped nanoparticles under pH-controlled conditions. The assemblies show a chain-like morphology, which results in a new NIR LSPR that is intimately related to the number of nanoparticles within the assemblies (Figure1). Furthermore, the proteins in the assemblies retain their biotin-binding properties, which makes it easy to decorate the assemblies with biotinylated molecules such as enzymes. The assemblies reconfigure into smaller clusters when the pH of the solution or the concentration of thiolated molecules increases, and therefore they can be programmed to adapt their NIR absorption as a function of these parameters.

The LSPR of the assemblies is directly related to the concentration of proteins added to the nanoparticles. This observation has allowed us to design a new signal generation mechanism for biosensing based on changing the concentration of neutravidin, and therefore the LSPR of the assemblies, with an immunoassay that uses biotinylated antibodies as biorecognition elements. Instead of using bulky spectrophotometers or unreliable naked-eye visualization for detecting changes in the extinction spectrum of the nanoparticles we have designed a new type of paper transducer that enables detecting such changes with an augmented reality app [4]. With this approach, we have been able to detect the model analyte C-reactive protein with a lower limit of detection than a conventional, non-portable ELISA.

References

[1] R. de la Rica and M. M. Stevens, Nat. Nanotechnol. 7 (2012) 821.
[2] S. A. Paterson, S. A. Thompson, J. Gracie, A. W. Wark and R. de la Rica, Chem. Sci. 7, (2016) 6232.
[3] R. de la Rica, Nanoscale 9 (2017) 18855.
[4] S. M. Russell, A. Doménech-Sánchez. R. de la Rica, ACS Sensors 2 (2017), 848.

Figures

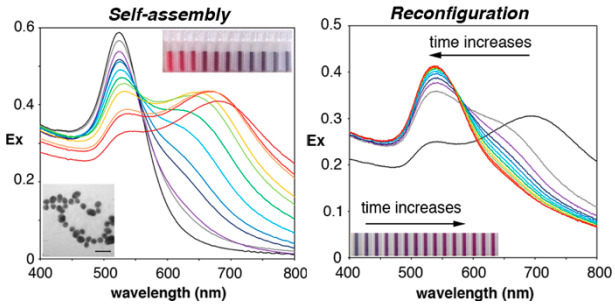

Figure 1: Figure 1: Assembly and reconfiguration of gold nanoparticles with chain-like morphologies. The key aspect to assemble the colloids is adding biotin-binding proteins at different concentrations. This can be used to

generate plasmonic signals in biosensors using biotinylated antibodies as recognition elements.